

# High Precision Ag Isotopic Measurements of Low Pd/Ag Meteorites

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**Introduction:** The now extinct radionuclide <sup>107</sup>Pd decays to <sup>107</sup>Ag with a half life of 6.5Myr. Highly volatile element depleted (i.e. high Pd/Ag) Group IVA iron meteorites show good correlations between excess <sup>107</sup>Ag and Pd/Ag. This strongly indicates the presence of live <sup>107</sup>Pd at the start of the solar system [1]. Pd is both more refractory and more siderophile than Ag. Hence condensation/evaporation processes in the nebula, as well as planetary core formation, may have caused the requisite early Pd/Ag fractionation necessary for the system to be useful as a chronometer. Isochrons determined for iron meteorites generally yield initial <sup>107</sup>Pd/<sup>108</sup>Pd in the range 1.5 - 2.5 x 10<sup>-5</sup> [1], and this was confirmed recently by Carlson and Hauri [2] who measured an initial <sup>107</sup>Pd/<sup>108</sup>Pd of (2.39 ± 0.26) x 10<sup>-5</sup> for the Group IA iron meteorite Canyon Diablo.

Primitive chondritic meteorites have received only limited study with regard to Pd-Ag systematics. Early investigations using TIMS were hampered by lack of precision (typically 10-20ε, where ε = [(sample/standard)-1]\*10000, and showed that, within error, the ordinary chondrites Rose City (H5) and Floyd (L4) were identical in Ag isotopic composition to the Ag isotopic standard NIST SRM 978a [1]. Improved analytical precision (±1.3ε, 2σ) obtained through the use of multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) [2] permitted analysis of the carbonaceous chondrite Allende (CV3). The results of their study [2] indicated that Allende is enriched in <sup>107</sup>Ag by between +4 and +6.5ε relative to the NIST Ag standard.

**Methodology:** Silver has only 2 naturally occurring isotopes and hence a Pd 'spike' has been used to externally normalise the Ag data for instrumental mass bias. This external normalisation used together with a standard bracketing technique [2], enables a reproducibility on <sup>107</sup>Ag/<sup>109</sup>Ag of ± 50 ppm (2σ) to be obtained for a pure Ag standard (> 50 ng of Ag). Another method of external normalisation, the Maréchal Technique [3], can also be used to effectively determine differences in the isotopic composition of Ag between samples and standards [4]. Because the isotopic data are sensitive not only to isobaric interferences, but also to matrix-induced changes in the instrumental mass fractionation behaviour of Ag relative to Pd [5], Ag must be efficiently separated from the sample matrix

using ion-exchange chromatography. Total Ag procedural blanks for the process, including sample dissolution in a high-pressure asher, are < 15 pg if high purity double distilled acids are used.

Correction of instrumental mass discrimination by external normalisation of Ag to Pd does not correct for the fractionation that occurs in nature or during sample processing [6]. Previous Ag isotopic studies [2] noted that apparent 'anomalies' (< 3ε) could be generated in the laboratory. The presence of chlorine in sample solutions can cause apparent isotopic shifts and samples should only be compared to fresh standards as standards can become isotopically lighter (ε<sup>107</sup>Ag increases) with time [4]. Recognition of these problems and refinement of the chemical separation procedure for Ag [2, 4] is believed to have improved the accuracy of Ag isotopic measurements by removing the source of certain analytical artifacts.

Our long term repeat analyses of a JMC Ag standard bracketed by NIST SRM 978a (<sup>107</sup>Ag/<sup>109</sup>Ag = 1.08038 ± 0.00043) reveal an isotopic difference of ε<sup>107</sup>Ag = ± 1.52 ± 0.44 (2σ; n = 25, where n is the number of measurements). This illustrates the ability of MC-ICPMS to reliably quantify small differences in isotope compositions.

**Results:** Terrestrial standards AGV-2 (andesite), SCO-1 (black shale) and a pure Ag ore all have Ag isotope compositions which are within error of the NIST Ag standard. For repeat analyses of SCO-1 (n = 8) the reproducibility attainable is ~ ± 1ε (2σ). Repeat analyses have also been made of the chondrites Allende (CV3) and Abee (EH4). Relative to NIST Ag, an average value for Allende of ε<sup>107</sup>Ag = -0.82 ± 1.38 (2σ, n = 4) has been measured. The average of 3 analyses of Abee yields ε<sup>107</sup>Ag = -0.52 ± 2.72 (2σ). This reproducibility is comparable to that obtained by [2] for replicate analyses of Allende, but it is slightly worse than that of the terrestrial standards. This may simply be due to sample heterogeneity problems inherent with small sample sizes. Therefore, an uncertainty of ± 1.5ε is applied to all unknown samples to reflect the range in reproducibility attainable for standards and samples.

Other meteorites analysed include the ordinary chondrites Guarena (H6), Ausson (L5), Tennašilm (L4), Mezö-Madaras (L3) and ALH 84081 (LL), the

carbonaceous chondrite Murchison (CM2), the enstatite chondrite Indarch (EH4) and the Group IA iron Canyon Diablo. All chondrites with the exception of ALH 84081 (which was analysed twice giving  $\epsilon^{107}\text{Ag} = +3.48$  and  $\epsilon^{107}\text{Ag} = +3.40$ ) overlap, within error, with the 'terrestrial' value of the NIST Ag standard (Figure 1).

A sample of Canyon Diablo containing both a large discrete sulphide bleb and metal was obtained and separate analyses of the sulphide and metal were carried out. The Ag isotopic composition of the metal is  $\epsilon^{107}\text{Ag} = +0.86$  and two replicate analyses of the sulphide give  $\epsilon^{107}\text{Ag} = -2.07$  and  $-1.54$ , respectively (Figure 1).

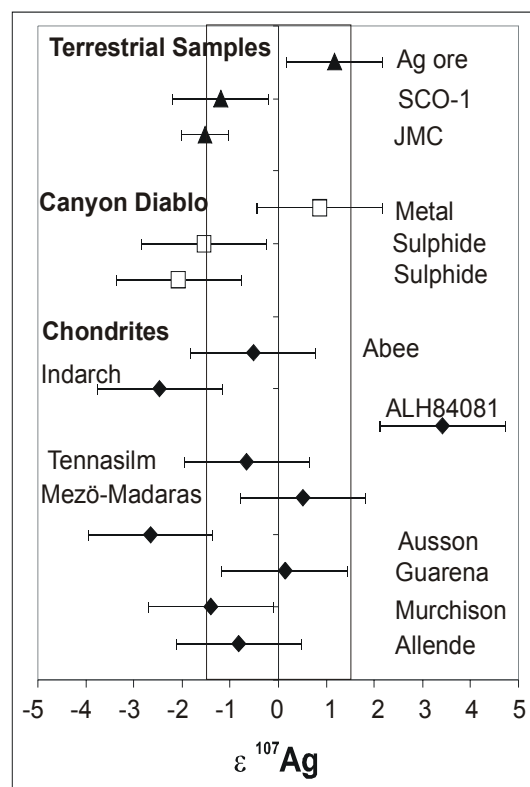
**Discussion:**  $^{108}\text{Pd}/^{109}\text{Ag}$  in most chondritic meteorites is  $< 10$  (with the exception of the H and EL groups). Thus, given the low initial  $^{107}\text{Pd}/^{108}\text{Pd}$  of the solar system [1], it is unlikely that any Ag isotopic anomalies due to  $^{107}\text{Pd}$  decay will be resolvable at current levels of precision. However, some volatility-related stable-isotope fractionation of Ag isotopes might have occurred across the accretion disk. The chondrites analysed cover a large area of the disk, from the highly reduced and volatile depleted inner part (enstatite chondrites), to the more oxidised and volatile rich outer part (carbonaceous chondrites), but, they all have identical Ag isotope composition. This suggests either that Ag isotopes are not a good proxy for the study of volatility-related isotope fractionation, or, that volatile element depletion within the accretion disk was not associated with Ag isotope fractionation.

The positive 'anomaly' measured for the LL chondrite ALH 84081 may reflect terrestrial alteration of the meteorite. Therefore, this analysis should be considered suspect until other non-antarctic LL chondrites have been analysed.

The new analyses of Allende do not replicate the positive anomaly of Allende relative to NIST Ag measured previously [2] ( $\epsilon^{107}\text{Ag} = +5.2$ ). Likewise, the very negative values measured for Canyon Diablo sulphide by [2] (ca.  $\epsilon^{107}\text{Ag} = -10.6$  to  $-13.7\epsilon$ ) were not replicated. However, the Ag isotopic composition of Canyon Diablo metal measured in this work and that of [2] are identical. Whether the differences are due to changes in the chemical separation procedure, differences in the mass spectrometry protocols or sample heterogeneity is unclear at present.

The measurements of Canyon Diablo sulphide by [2] give the lowest  $^{107}\text{Ag}/^{109}\text{Ag}$  yet measured for solar system material and have been used to estimate the initial solar system  $^{107}\text{Ag}/^{109}\text{Ag}$ . A line fit through the Allende and Canyon Diablo sulphide data of [2] gen-

erates a very high solar system initial  $^{107}\text{Pd}/^{108}\text{Pd}$  of  $39 \times 10^{-5}$  for Allende [2]. This cannot easily be reconciled with other Pd-Ag isotope data without invoking the presence of nuclear anomalies [2]. The results of this study, however, indicate that both Allende and Canyon Diablo sulphide may have less extreme Ag isotopic compositions. A best-fit line through the new data (using values of  $^{108}\text{Pd}/^{109}\text{Ag}$  from [2]) produces an initial  $^{107}\text{Pd}/^{108}\text{Pd}$  of  $< 5 \times 10^{-5}$ . This value is more in accord with previous estimates based on iron meteorites [1, 2].



**Figure 1.** Ag isotopic data for chondrites, terrestrial standards and the iron meteorite Canyon Diablo. All data are normalised to bracketing NIST SRM 978a. Error bars of  $\pm 1.5\epsilon$  are applied to all data except for the JMC std (error =  $\pm 0.44 \epsilon$ ).

**References:** [1] Chen J. H. and Wasserburg G. J. (1996), in *Earth Processes: Reading the Isotopic Code*, Geophysics Monograph 95, pp 1-20. [2] Carlson R. W. and Hauri E. H. (2001), *Geochim. Cosmochim. Acta*, 65: 1837-1848. [3] Maréchal C. N., et al. (1999), *Chem. Geol.*, 156: 251-273. [4] Woodland S. J. et al. (*in press*), *Plasma Source Mass Spectrometry, R.S.C.* [5] Carlson R. W. et al. (2001), in *Plasma Source Mass Spectrometry: The New Millennium*, p 288-293. [6] Rehkämper M. et al. (*in press*), *Handbook of Stable Isotope Analytical Techniques*.